ABSTRACT

Title of thesis: TRACKING TRANSPORT OF 'CHEMICAL COCKTAILS' OF TRACE METALS USING SENSORS IN URBAN STREAMS

Carol Morel, Masters of Geology, 2020

Thesis directed by: Professor Sujay Kaushal
Department of Geology

Understanding transport mechanisms and temporal patterns in metals concentrations and fluxes in urban streams are important for developing best management practices and restoration strategies to improve water quality. In some cases, *in situ* sensors can be used to estimate unknown concentrations and fluxes of trace metals or to interpolate between sampling events. Continuous sensor data from the United States Geological Survey were analyzed to determine statistically significant relationships between lead, copper, zinc, cadmium and mercury with turbidity, specific conductance, dissolved oxygen, and discharge for the Hickey Run, Watts Branch, and Rock Creek watersheds in the Washington, D.C. region. At Rock Creek, there were significant negative linear relationships between Hg and Pb and specific conductance ($p<0.05$). Watershed monitoring approaches using continuous sensor data have the potential to characterize the frequency, magnitude, and composition of pulses in concentrations and loads of trace metals, which could improve management and restoration of urban streams.

TRACKING TRANSPORT OF ‘CHEMICAL COCKTAILS’ OF TRACE METALS USING SENSORS IN URBAN STREAMS

by

Carol Jisnely Morel

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Advisory Committee:

Professor Sujay Kaushal, Chair
Dr. Kenneth Belt
Dr. Shuiwang Duan
Professor Karen Prestegaard

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Introduction

Urbanization is expected to increase over the next century with significant impacts on water quality in streams and rivers across space and time (Grimm et al. 2008, Walsh et al. 2005, Kaushal and Belt 2012, Kaushal et al. 2020). Metals such as lead (Pb), cadmium (Cd), copper (Cu), zinc (Zn), and mercury (Hg), are commonly found together at elevated concentrations in many urban streams (*e.g.*, Characklis et al., 1997, Mahler et al., 2005, Franz et al., 2014, Kaushal et al. 2020). Urbanization has significant impacts on transport and transformation of novel mixtures of these and other metals, which can form 'chemical cocktails' in many watersheds across regional and global scales (Kaushal et al. 2018a, Kaushal et al. 2019 Kaushal et al. 2020). Tracking changes in concentrations and fluxes of metal cocktails in urban streams is important for predicting impacts on aquatic life, ecosystem functions, and human health (*e.g.*, Characklis et al., 1997; Mahler et al., 2005; Trombulak et al., 1999). Rapid fluctuations in concentrations and fluxes of metals are sometimes difficult to track in urban streams, which can occur over short time scales in response to hydrologic events (Hunter et al. 1981; Weibel et al. 1964; Whipple and Hunter 1977). In this work, I explore changes in metal concentrations across three urban watersheds varying in size and impervious surface cover, and analyze relationships between trace metals and in-stream continuous sensor data (turbidity, dissolved oxygen, specific conductance, pH, temperature, and discharge). Analyzing concentrations of metals in urban watersheds and relationships between sensor data and multiple metals can provide insights on tracking the transport of complex chemical mixtures in urban streams.

Many metals undergo a range of rapid transport and transformation processes due to aqueous chemical reactions, particularly before, during, and after storm events (Stumm and Morgan, 1996). Previous studies indicate positive correlations between metals contamination and

urban land use; frequent floods and storm events enhance metal mobility and lead to environmental and public health risks (Characklis et al., 1997; Franz et al., 2014; Lee et al., 2000; Mahler et al., 2005; Mason et al., 1998; Tiefenthaler et al., 2009; Wheeler et al., 2005; Defo et al, 2015). Urban areas have a much higher percentage of impervious surfaces, which can allow for metals to be transported to local streams and rivers more efficiently *via* runoff. For example, urban drainage networks can act as channeled conduits for direct inputs of metals into nearby streams, and the erosional power of stormwater flow can allow for greater overall transport of metals in particulate form (Kaushal and Belt 2012, Kaushal et al. 2020).

Metals can be rapidly transformed by processes including organometallic complexation and sorption to sediments; these transformations could be tracked by sensors (Stumm and Morgan, 1996, Hsu et al., 2003). In seasonally cold regions, salinization from road salts can affect metal transport by increasing their solubility due to anion complexation and divalent cation competition, which can increase the concentration of total dissolved metals in solution *via* the 'salting in' effect (Kaushal et al., 2019; Schwarzenbach, et al., 2013). 'Salting in' relates to the formation of more soluble and labile compounds *via* anion complexation. Divalent cation competition displaces metals adsorbed onto sediments, which makes them more mobile (Schwarzenbach, et al., 2013). Similarly, some metals may be released into solution from iron and manganese oxyhydroxides in response to changes in redox conditions, and would be sensitive to fluctuations in dissolved oxygen (Davranche & Bollinger, 2000; Stumm et al., 2003). Using sensor data to estimate metal concentrations is possible if there are significant statistical relationships between metals concentrations and sensor parameters such as turbidity, dissolved oxygen, specific conductance and discharge. Sensors measure continuously and can track rapid changes in environmental

parameters that could be used to evaluate whether stream maximum contaminant limits have been exceeded.

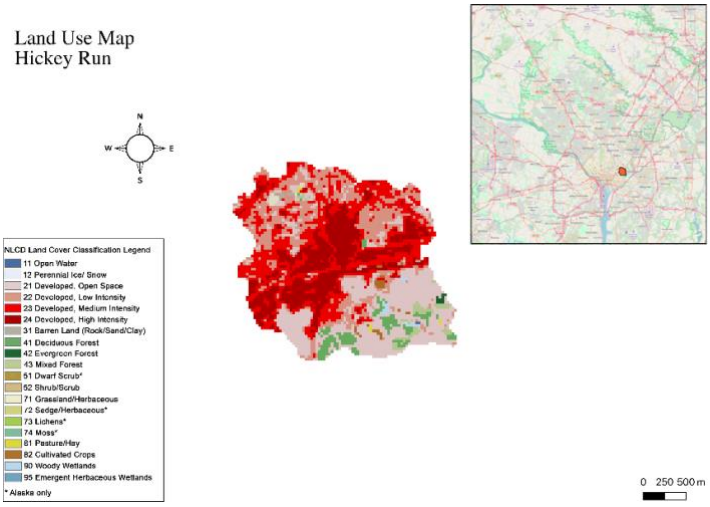
My work focused on analyzing relationships between metals (lead, copper, zinc, cadmium and mercury) concentrations and in-stream sensor data such as turbidity, dissolved oxygen (DO), specific conductance (SC), pH, temperature (Temp) and discharge (Q). Concentrations of metals were analyzed from discrete sampling events across urban watersheds. I used a data base collected by the United States Geological Survery (USGS) from three urban streams in the Washington DC metropolitan region. Concentrations of metals in streams are regulated for safe drinking water and protection of aquatic life in the U.S. (US EPA, 2015). Analyzing and predicting the high-frequency resolution dynamics of metals in urban streams over time is difficult due to labor intensive sampling and costly geochemical analyses; there is currently a dearth of cost-effective and reliable alternatives. Environmental variables measured continuously by *in situ* sensors can potentially serve as robust proxies for metals concentrations, allowing for estimation of peaks in metals concentrations and loads during storms and regulatory exceedances. However, this has been less explored for multiple metals, and there may be limitations and uncertainties, which need to be identified. Predicting frequency and magnitude of water quality exceedances of metals in urban watersheds *via* the use of continuous sensor data as proxies could improve monitoring and management of metals in urban watersheds and also identify potential limitations in relying on traditional sampling approaches

Site Descriptions

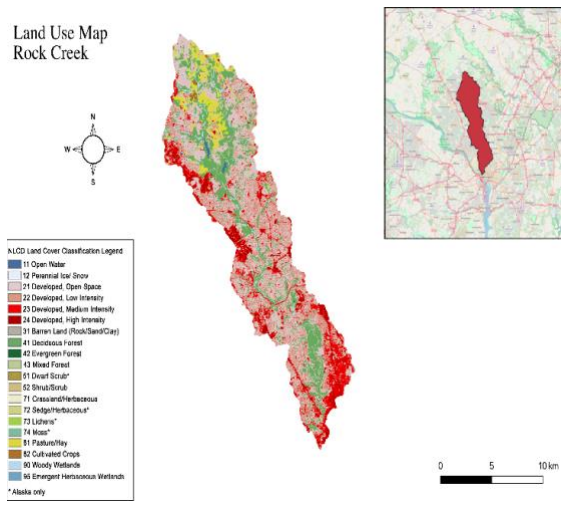
Continuous sensor data and metals concentrations from three separate watersheds in the Washington, DC, area were analyzed from the USGS National Water Information System. These

three watersheds were: Rock Creek at Joyce Road (USGS 01648010), Watts Branch (USGS 01651800) and Hickey Run (USGS 01651770) (Figure 1).

Figure 1. Land use for the Rock Creek, Hickey Run, and Watts Branch watersheds.



(a)



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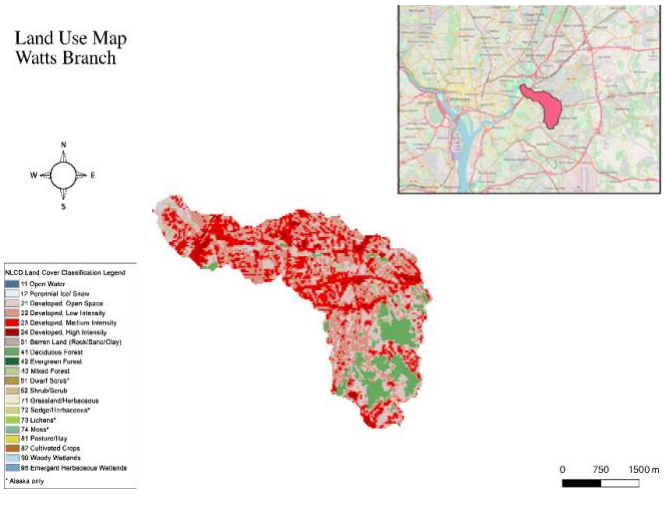


(c)

While all located in the DC metropolitan area, the aforementioned watersheds vary in drainage area, percentage of impervious surfaces, proximity to potential point sources (sites with

National Pollutant Discharge Elimination System (NPDES) or Municipal Separate Storm Sewer System Permits (MS4)) and land use distribution (Table 1). The Rock Creek watershed and its tributaries, specifically, have set Total Maximum Daily Loads (TMDLs) for arsenic, copper, lead, mercury, and zinc.

Table 1. Watershed characteristics table for the Rock Creek, Hickey Run and Watts Branch watersheds.

Water-shed	Drainage area (square miles)	Percent impervious surface	Dominant land use	# of potential point sources within the watershed	Dominant metal of concern	Other contaminants of concern	Direction of effluent
Rock Creek	63.7	32.4%	Residential (45%)	3	Lead	Fecal coliform bacteria, mercury, zinc, copper, arsenic	Potomac
Watts Branch	3.36	41.4%	Residential (73.2)	0	Arsenic	Organic pollutants, arsenic, copper, chlordane	Anacostia

Hickey Run	0.99	52.7%	Parkland (34%)	0	Zinc	Arsenic, organic pollutants, copper	Anacostia

Rock Creek is one of the major streams in the Washington D.C. area. The 33-mile creek, with drainage area of 63.7 square miles, extends from Laytonsville, Maryland, to the Potomac River in the District of Columbia. In the 1890's, a large portion of the Rock Creek river valley was designated to become one of the nation's first national park (Rock Creek Conservancy, 2019). As population rapidly grew during the 1940's and 1950s, forests and farmlands were converted to suburban developments, which adversely affected water quality as storm sewer systems diverted runoff directly into the creek (Rock Creek Conservancy, 2019). The 64 square mile watershed now comprises of 45% residential, 31% grassland, 23% agriculture and recreational, and 2% wetlands (District Department of the Environment Watershed Protection Division, 2010). After complaints filed by third party interests in 2009, revisions have been made to the total maximum daily loads to better reflect its current state in water quality. Studies have shown that fecal coliform, mercury, copper, zinc, and lead are major contaminants of concern in this tributary (DC Department of Energy & Environment, 2016).

Watts Branch is a small watershed (3.36 mi^2) tributary to the Anacostia River. It begins in Prince George's County, MD and joins the Anacostia R. in Kenilworth Park. Land use consists of 73.2% residential areas, 11% forested areas, 8.2% open space, 7.3% government lands, and 0.3% wetlands (U.S. Fish & Wildlife Service, 2003). In the 19th century, a vast majority of the

watershed was converted from forests and meadows to croplands (U.S. Fish & Wildlife Service, 2003). After World War II, deforestation rates increased in order to develop residential and industrial areas (U.S. Fish & Wildlife Service, 2003). During the 1980's, much of the land became urbanized. As a result of the increased impervious surfaces, total suspended sediment loads significantly increased, calling for a national restoration effort (U.S. Environmental Protection Agency, 2013). Along with sediment loads, pollutants like lead, organic pollutants, copper, and arsenic also became major contaminants of concern in the watershed. Sediment loads have been reduced by 33% since the 1990's due to the efforts stemming from the Watts Branch Project (U.S. Environmental Protection Agency, 2013). Despite significant reductions in bank erosion, storm water and nutrient runoff, Watts Branch is still listed impaired as of 2018 due to high organic pollutant, metal, and bacteria levels (Department of Energy and Environment, 2018). DDOE is addressing these concerns by conducting ongoing monitoring to ensure water quality improvement (U.S. Environmental Protection Agency, 2013).

Hickey Run is also a small tributary of the Anacostia River, located within the District of Columbia. The 1 km^2 watershed contains 34% parkland, 30% industrial, and 29% residential (Anacostia Watershed Restoration Partnership, 2019). It was also deforested as population increased to provide for suburban and residential developments (U.S. Fish & Wildlife Service, 2003). In the early 1900s, the stream has been a waste site for grease and oil discharge (District Department of the Environment Natural Resources Administration Water Quality, 2014). Water quality became a concern in the 1930's when the stream caught on fire after decades of pollution. Currently, it is one of the most altered watersheds in the Anacostia River, with 41% of the watershed covered by impervious surfaces (Anacostia Watershed Restoration Partnership, 2019). Watts branch water quality is restoration challenge for the District Department of the Environment

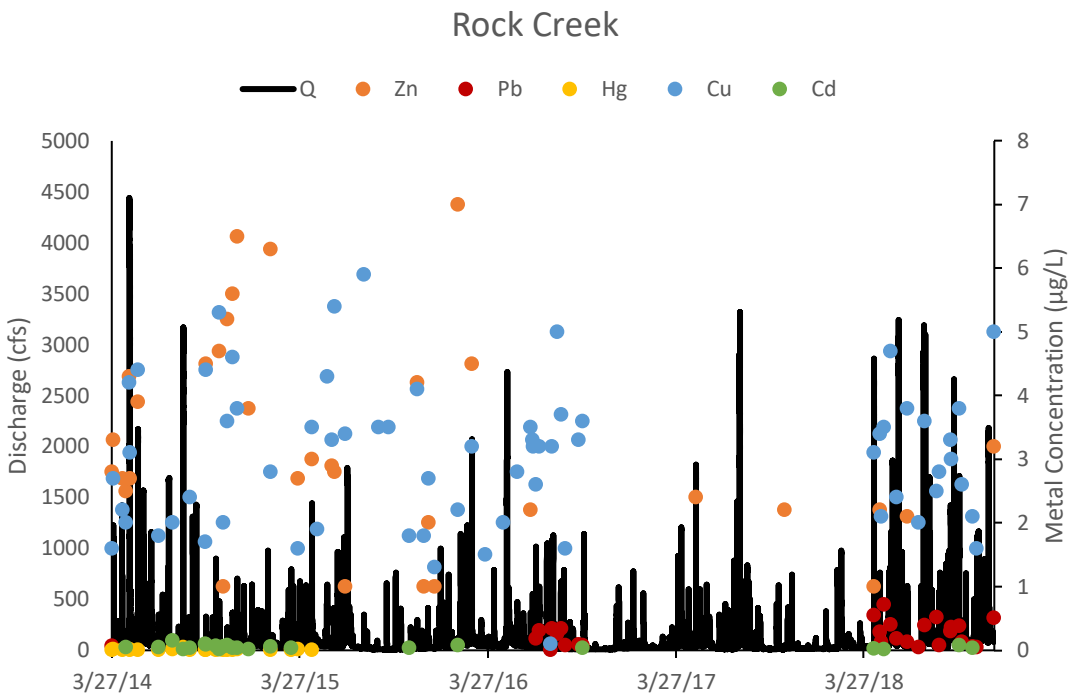
as they try to reduce stormwater runoff and hydrocarbon pollution (Anacostia Watershed Restoration Partnership, 2019). Major pollutants of concern include organic pollutants, copper, zinc, and arsenic (District Department of the Environment Natural Resources Administration Water Quality, 2014). Restoration efforts are focused on stormwater management, revising total maximum daily load standards, wetland creation, and providing incentives for homeowners to get involved with storm water management (Department of Energy & Environment, 2019). As a result, there has been an increase in landscape enhancements such as rain barrels, rain gardens, and shade trees designed to reduce stormwater runoff (Department of Energy & Environment, 2019).

Methods

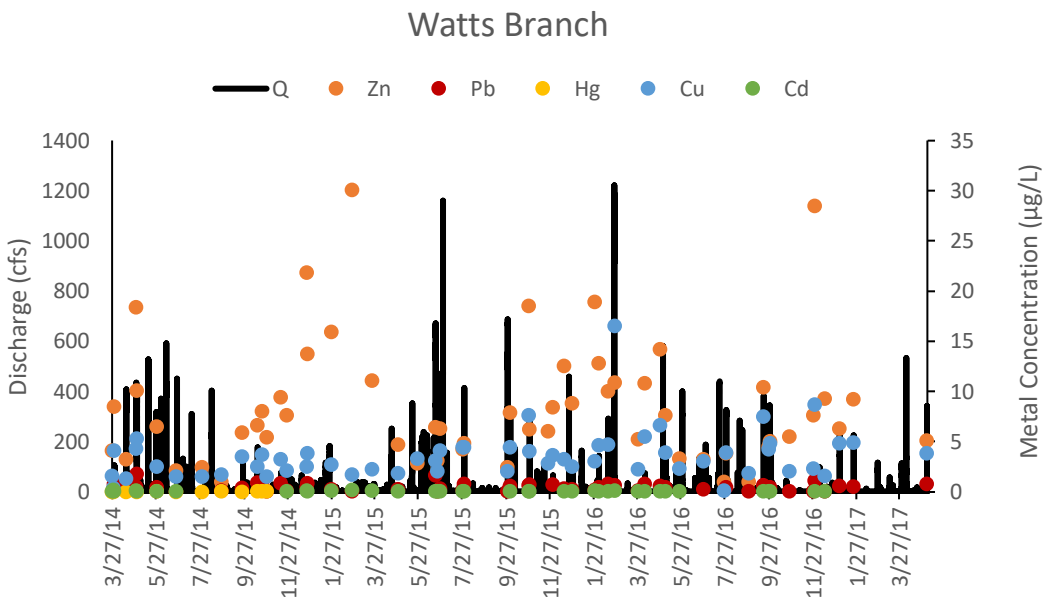
Discrete Sampling for Metals by the USGS

In 2013, the USGS started a project in collaboration with the EPA and DC's Department of Energy and the Environment to enhance Non-Tidal Network monitoring by adding analytes such as trace metals and mercury at poorly represented small, urban catchments in the DC area. Both storms and fixed frequency samples are collected on a monthly basis (Webber et al.) Water samples are collected and analyzed for dissolved metals. At all three sites, monthly sampling for metals is conducted for discharges ranging from baseflow to stormflow, including the intervals during and after storms (Figure 2).

Figure 2. Sampling of metals over discharge for the Rock Creek, Hickey Run, and Watts Branch watersheds.


Rock Creek
Q
Zn
Pb
Hg
Cu
Cd
Discharge (cfs)
Metal Concentration (µg/L)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
8
7
6
5
4
3
2
1
0
3/27/14
3/27/15
3/27/16
3/27/17
3/27/18

(a)


Watts Branch
Q
Zn
Pb
Hg
Cu
Cd
Discharge (cfs)
Metal Concentration (µg/L)
1400
1200
1000
800
600
400
200
0
35
30
25
20
15
10
5
0
3/27/14
5/27/14
7/27/14
9/27/14
11/27/14
1/27/15
3/27/15
5/27/15
7/27/15
9/27/15
11/27/15
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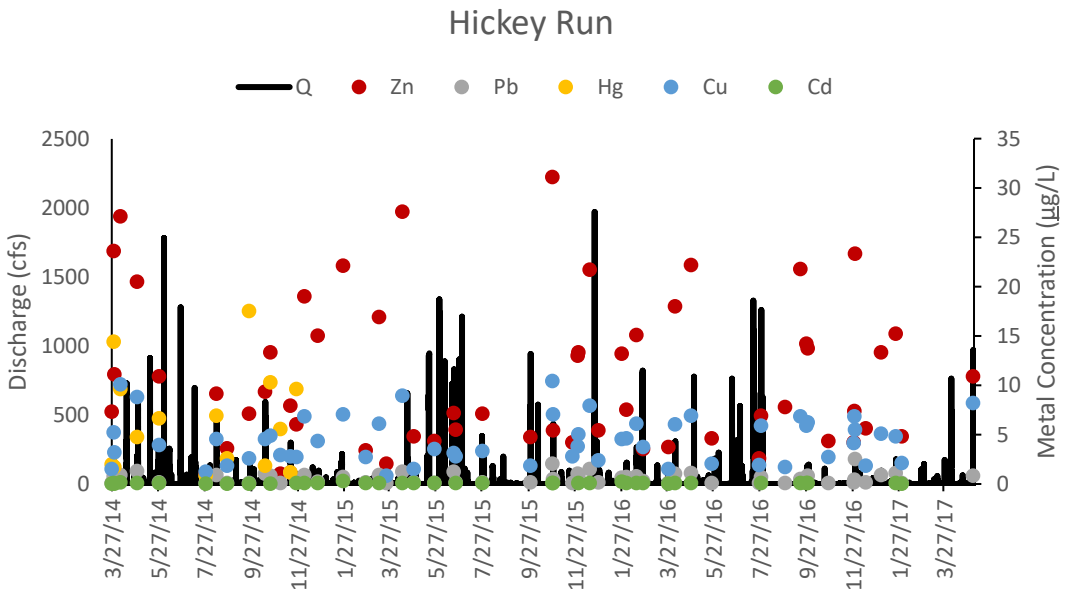
3/27/17

(b)



(c)

Water samples for all metal analyses (except for mercury) are filtered through a 0.45 – micrometer pore-size disposable capsule filters in the field (Wilde, 2002). All water samples are acidified with acid in the field by the USGS (Wilde, 2002). For major and minor cations and trace elements, nitric acid is added until the pH of the sample was below 2. Two milliliters of 6N ultrapure HCl are added to samples designated for mercury analysis (Wilde, 2002). Water samples are then analyzed on an Inductively Coupled Plasma Mass Spectrometer with reporting limits of 1 µg/L (Arbogast, 1996). Data collected from March 2014 through May 2018 were used. Data points that were known to be less than the reported value were assumed to be half the value of the detection limit (*i.e.*, midway between the detection limit and 0). Due to assumptions with samples near the detection limits, all statistical relationships derived from these data used only data points above the detection limits.

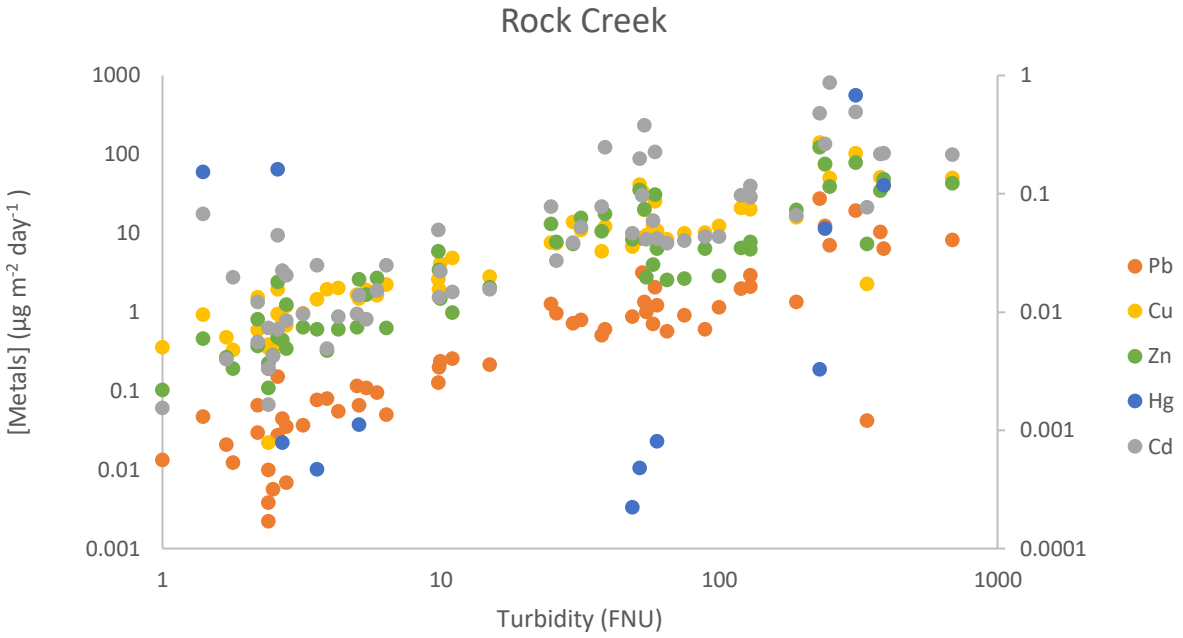
Stream Water Quality Sensors

The three selected USGS gage stations are equipped with sensors to continuously measure water quality parameters such as temperature, specific conductance, DO, pH and turbidity. Temperature is measured with a thermistor that can read within 0.1 degree Celsius of the actual temperature of the stream (Wagner et al., 2006). Specific conductance is measured as micro-siemens per centimeter at 25 degrees Celsius using contact sensors with electrodes that measure in the range of 0-2000 uS/cm (Wagner et al., 2006). Dissolved oxygen is measured using the amperometric method. The amperometric method uses a temperature-compensated polarographic membrane-type sensor. Continuous water quality pH sensors employ the electometric pH-measurement method, which uses a hydrogen-ion electrode (Wagner et al., 2006). This electrode can accurately measure pH within 0.2 pH units. Submersible turbidity sensors used by the USGS emit a light beam from a light-emitting diode into the water and measure the light that scatters or is absorbed (Wagner et al., 2006). Turbidity sensors typically have a range of 0-1000 nephelometric turbidity units (NTU) with an accuracy of 2 NTU or within 5%.

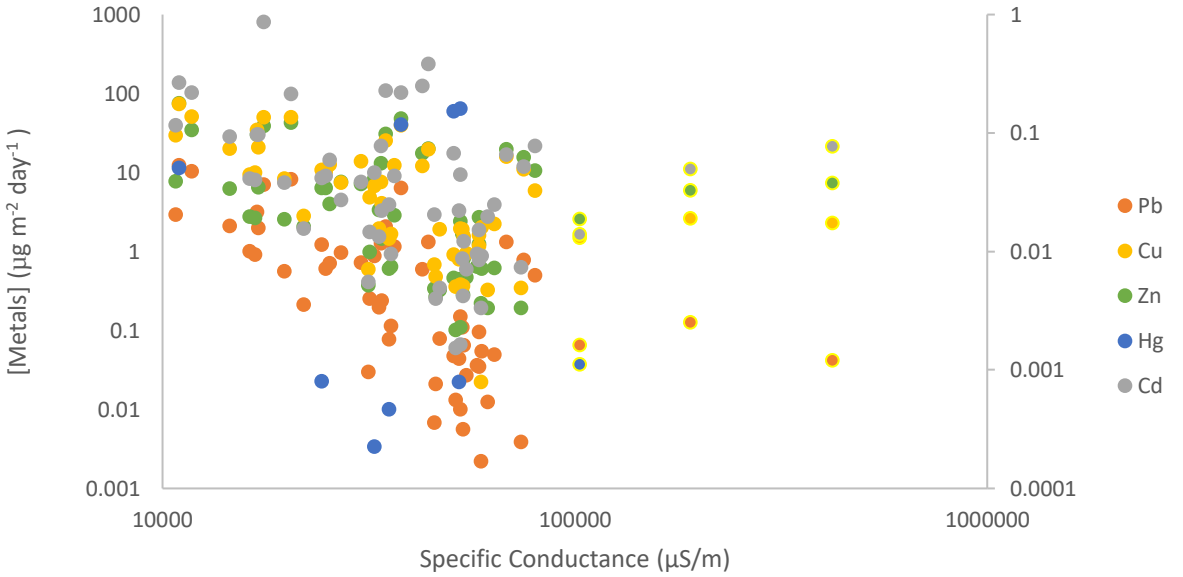
Statistical Analyses of Relationships between Water Quality Parameters and Metals

A variety of statistical tests were used to compare metal concentrations among the sites and to develop statistical relationships between metal fluxes and water quality parameters. These methods included: a) box and whisker plots of normalized data (fluxes normalized by drainage basin area), b) multiple linear regression, to compare fluxes and concentrations among the sites, and (c) regression relationships between metal concentrations and environmental parameters. Relationships between metal fluxes and turbidity, specific conductance and instantaneous discharge were plotted in Figure 3.

Figure 3. Relationships between metal fluxes and turbidity, specific conductance and instantaneous discharge for the Rock Creek, Hickey Run, and Watts Branch watersheds.



(a)



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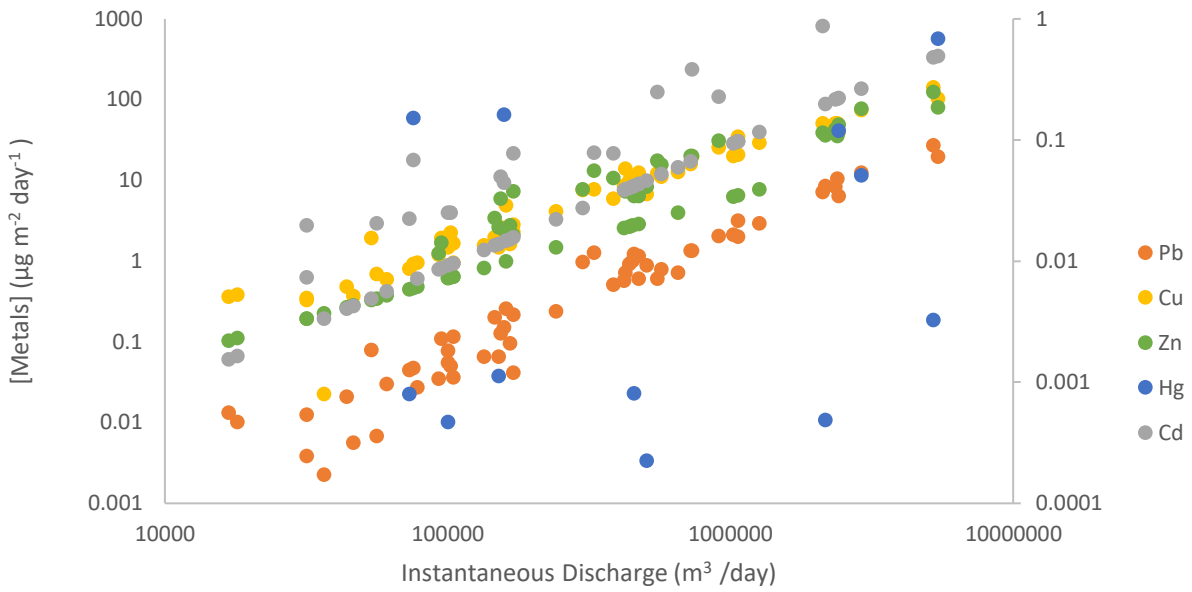
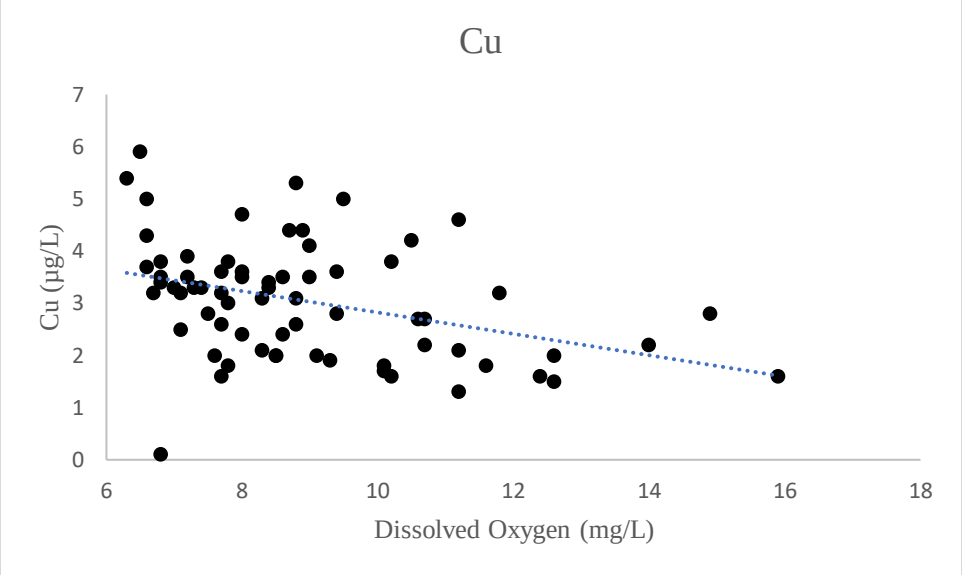


(c)

Metal concentrations for Cu were plotted against dissolved oxygen as well (Figure 4).

Figure 4. Relationship between copper and dissolved oxygen at the Rock Creek watershed (R_2 = 0.14).



Box and whisker plots were generated to compare concentrations and fluxes of trace metals across sites and analysis of variance tests (ANOVAs) were performed to check for statistical differences. Non-metric Multidimensional Scaling analysis was also conducted to spatially assess similarities and differences between sites. Then, multiple linear regression (in the statistical program R) was used to assess the contribution of each predictor variable (continuous sensor data) to the response variable (metals concentrations) for each site. All parameters available for each site were used to define the model. Data were standardized and checked for normality using the Shapiro Wilk Normality test using the *'ggplot'* and *'qqplot'*.

Multicollinearity (when two or more independent explanatory variables have a correlation of 1 or -1) of the multiple regression models was assessed using the variance inflation factor (VIF) function; this function will be repeated until all values are below 10 (multicollinearity is highly suggested above 10). After normality and collinearity have been checked, the model is run through the '*glmulti'* function that computes the Akaike information criterion (AIC) for several models and finds the best model to fit the data. The '*glmulti'* function also corrects for small sample sizes. The model with the lowest AIC is considered the best model as defined by the equation

(-2)log-(L)+2(K) (equation 1).

where L is the maximum likelihood and K is the number of independently adjusted parameters within the model. The AIC does not choose a model based on absolute quality, but will choose the best model available. The delta score for the AIC model is the difference in AIC between the best model and each other model in the set; according to Burnham and Anderson (2004), a delta score of less than or equal to 2 gives substantial evidence for the model. The model developed using the larger Rock Creek Data set was then used as a template for Watts Branch and Hickey Run. In

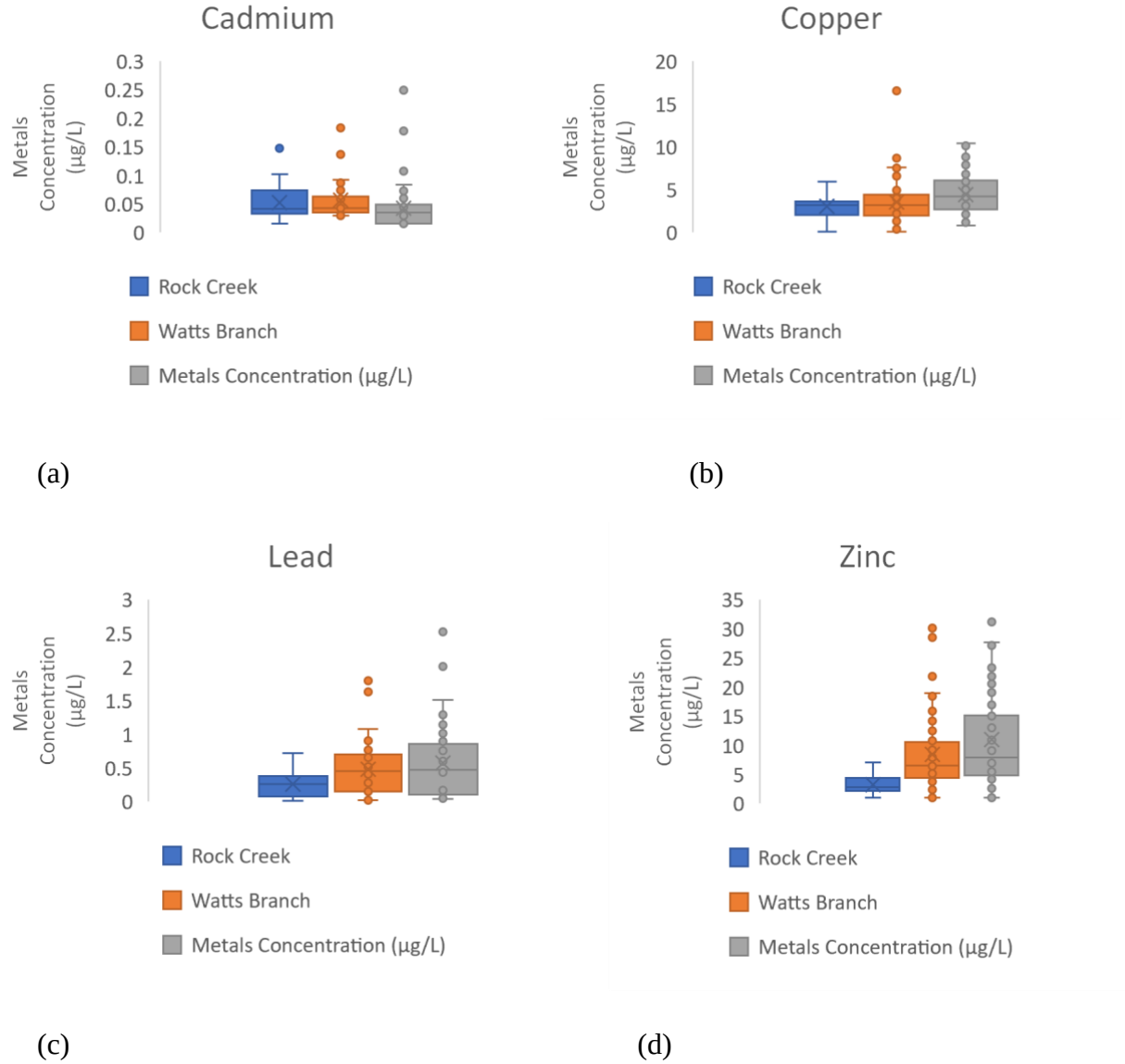
addition, single linear regression models were developed for predicting concentrations of individual metals to assess the ability of single sensors to predict metals concentrations.

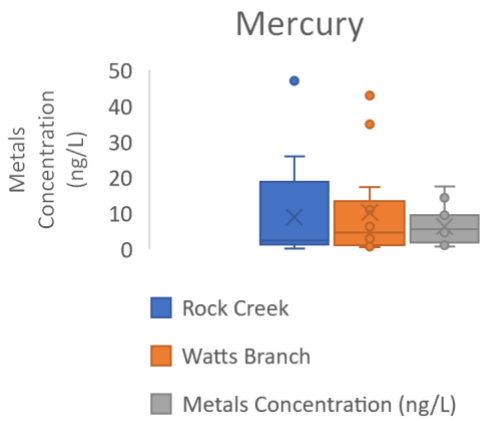
Results

Comparing Concentrations, Fluxes, and Mixtures of Trace Metals among Sites

Metals concentrations varied by several orders of magnitude at each site (Figure 5).

Figure 5. Concentrations of each metal for the Rock Creek, Hickey Run, and Watts Branch watersheds.

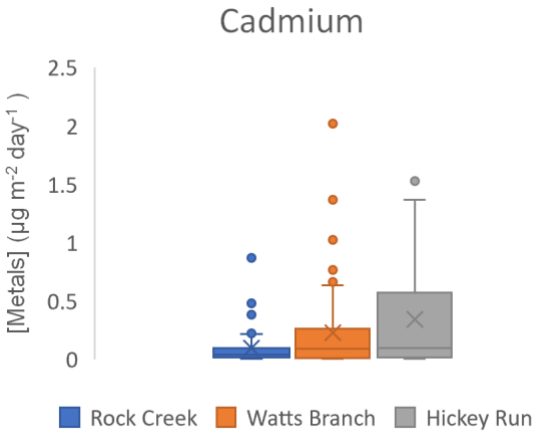




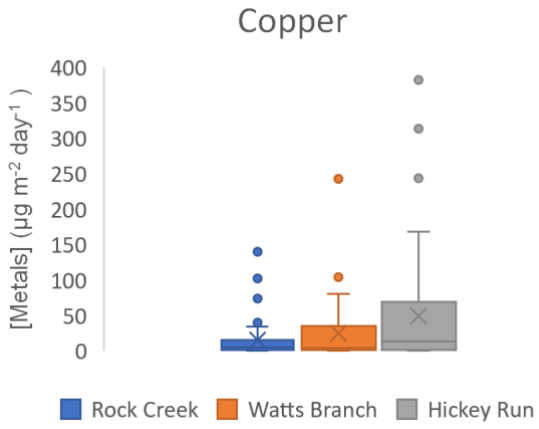
(e)

For example, Cu concentrations ranged from 0.25 to 2,934 ppb in Hickey Run over the sampling period. Concentrations of Pb peaked at 27, 290, and 1,134 ppb at Rock Creek, Watts Branch, and Hickey Run respectively. Daily fluxes for metals concentrations across sites are plotted in Figure 6 and their respective ranges in data are displayed in Tables 2-4.

Figure 6. Daily fluxes of metals for the Rock Creek, Hickey Run, and Watts Branch watersheds.



(a)



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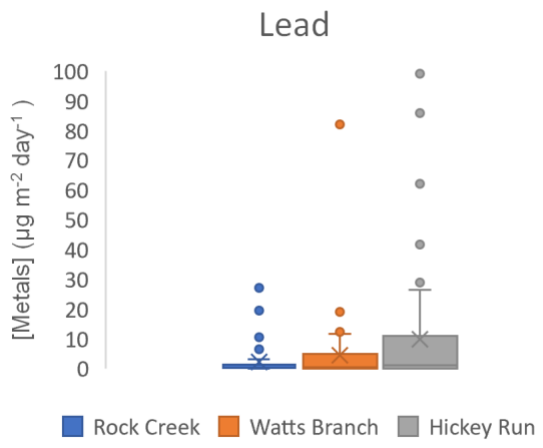

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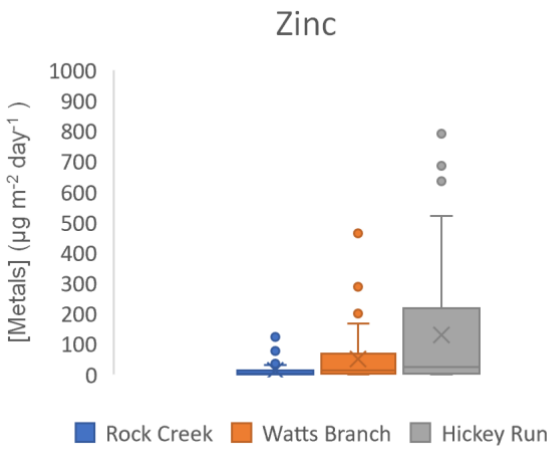

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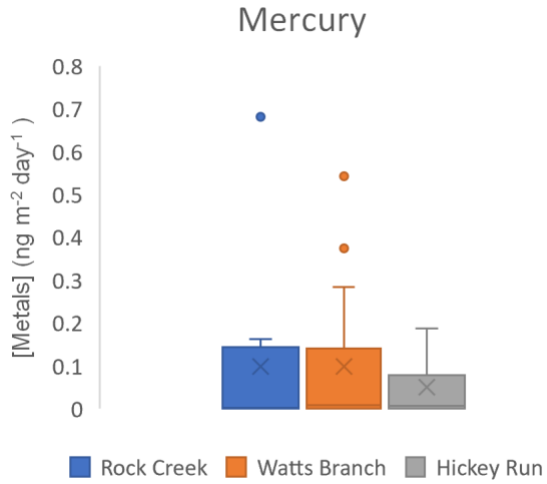


(e)

Table 2. Table of max, median, mean, standard error of the mean (SEM), min and quartiles for daily flux concentrations at the Rock Creek watershed.

Rock Creek	**Cu (µg m-2 day-1)**	**Cd (µg m-2 day-1)**	**Pb (µg m-2 day-1)**	**Zn (µg m-2 day-1)**	**Hg (ng m-2 day-1)**
Max	140	0.865	27.2	124	0.682
median	4.89	0.040	0.254	2.74	0.002
mean	15.2	0.092	2.18	12.7	0.098
SEM	3.40	0.020	0.642	3.01	0.056
min	0.022	0.002	0.002	0.102	2.25E-04

first quartile	1.39	0.012	0.047	0.608	0.001
second quartile	4.89	0.040	0.254	2.74	0.002
third quartile	17.7	0.095	1.33	14.3	0.157

Table 3. Table of max, median, mean, standard error of the mean (SEM), min and quartiles for flux concentrations at the Watts Branch watershed

Watts Branch	**Cu (µg m^{-2} day^{-1})**	**Cd (µg m^{-2} day^{-1})**	**Pb (µg m^{-2} day^{-1})**	**Zn (µg m^{-2} day^{-1})**	**Hg (ng m^{-2} day^{-1})**
max	551	6.40	290	1140	0.543
median	3.88	0.101	0.445	12.7	0.008
mean	33.5	0.330	9.24	69.2	0.098
SEM	5.50	0.052	1.51	10.8	0.046
min	0.021	0.002	0.002	0.115	7.72E-05
first quartile	1.00	0.010	0.031	1.63	2.46E-04
second quartile	5.16	0.101	0.445	23.0	0.008
third quartile	37.7	0.262	5.86	83.7	0.284

Table 4. Table of max, median, mean, standard error of the mean (SEM), min and quartiles for flux concentrations at the Hickey Run watershed

Hickey Run	**Cu (µg m^{-2} day^{-1})**	**Cd (µg m^{-2} day^{-1})**	**Pb (µg m^{-2} day^{-1})**	**Zn (µg m^{-2} day^{-1})**	**Hg (ng m^{-2} day^{-1})**
max	2930	14.2	1170	6820	0.187
median	14.7	0.105	1.41	30.3	0.006
mean	99.2	0.582	29.8	244	0.050
SEM	10.3	0.060	2.60	25.0	0.018
min	0.258	0.003	0.010	0.258	3.18E-04
first quartile	0.858	0.0121	0.043	2.22	7.56E-04
second quartile	13.7	0.095	0.989	23.1	0.005
third quartile	74.3	0.719	11.6	245	0.098

Concentrations of all metals, with the exception of cadmium, appeared to increase with increasing impervious surface cover (Figure 5). No metal exceeds its maximum or secondary maximum contaminant limit as regulated by the U.S. Environmental Protection Agency.

ANOVAs were used to test for statistical differences among mean concentrations of each metal at each site (Table 5).

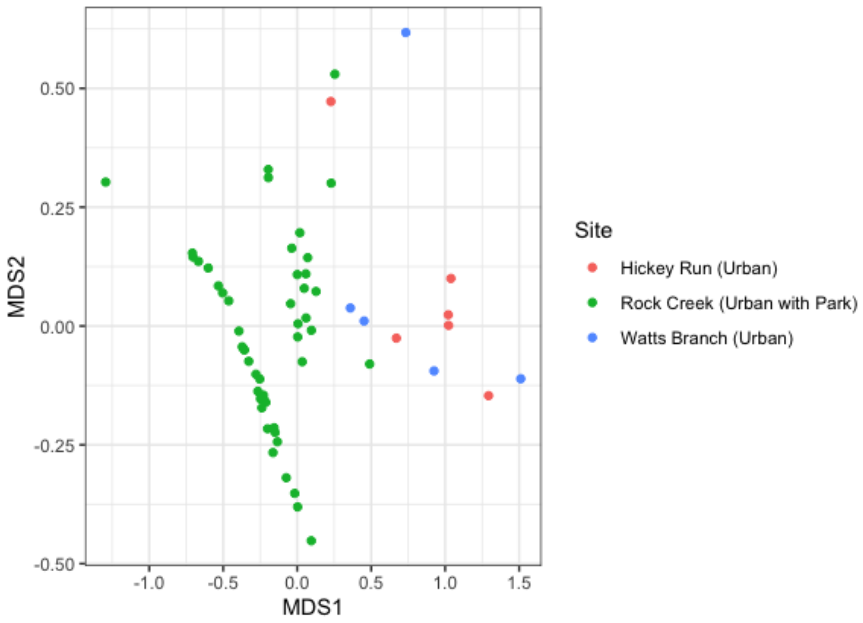
Table 5. ANOVA results for the Rock Creek, Hickey Run, and Watts Branch watersheds where DF is degrees of freedom and F is the F-statistic.

Source	*DF*	*F*	*P-value*	*F critical*
Cu	98	0.156	0.856	3.091
Cd	185	7.678	0.001	3.045
Hg	52	0.516	0.600	3.183
Pb	136	5.462	0.005	3.064
Zn	149	17.289	0.000	3.058

The results indicate a significant difference in mean concentrations for Cu and Hg across the three sites (F was less than F critical). No significant differences were found for concentrations of Pb, Zn and Cd across the three sites (F was greater than F critical); for instance, the calculated F statistic for Pb was 5.462 and F critical was 3.064. The p-value was greater than 0.5 for Cu and Hg.

The differences in metals concentrations were visualized using Non-metric Multidimensional Scaling (NMDS) (Figure 7).

Figure 7. Non metric multidimensional scaling plot for Rock Creek, Hickey Run and Watts Branch watersheds



NMDS is a rank-based approach where objects more similar to each other are ordinated closer together (Lefcheck, 2012). The two small watersheds with larger impervious surface cover, Watts Branch and Hickey Run, were more similar to each other than to Rock Creek, which had more forested parkland (Figure 7). Watts Branch and Hickey Run were also more similar in mean metals concentrations for Cu, Cd, Pb and Zn (Figure 5) (Table 1).

Relationships between Metals Concentrations and Continuous Sensor Data

Each metal, Cd, Cu, Zn, Pb, and Hg, for Rock Creek, Watts Branch and Hickey Run was analyzed against available continuous sensor parameters such as turbidity, temperature (T), specific conductance (SC), pH, dissolved oxygen (DO), and discharge (Q) to assess the contribution of each predictor variable to the response variable**.** Examples of relationships between metals concentrations and fluxes and turbidity, specific conductance and discharge are plotted in Figure 3. Metals concentrations and dissolved oxygen for Rock Creek are plotted in Figure 4. Discharge has a strong positive relationship with most metals fluxes (Figure 3c). Turbidity also

appears to have a positive relationship with fluxes of the aforementioned metals (Figure 3a). Specific conductance appears to show a weak negative correlation with concentrations of all metals at all sites (Figure 3b), although this relationship is bifurcated as at higher ranges of specific conductance, it appears that metal fluxes are increasing. However, this relationship was not statistically significant *via* a t-test for Cd and Zn for Rock Creek.

Evaluating Proxies for Metals Concentrations using Multiple Sensors

We only consider and report statistical relationships where R^2 values are greater than 0.70 as robust statistical models for predicting metals concentrations for using multiple linear regression analyses and AIC. For example, the mercury model for Rock Creek explained about 78% of the variability in the data and had an evidence weight of 30% (Table 6).

Table 6. Multiple linear regression models chosen with Akaike's Information Criterion predicting metals concentrations for Rock Creek, Watts Branch and Hickey Run watersheds. Rank is the model rank relative to all possible models, Wi is the weighting evidence or the probability of that model being the best model, and the adjusted R^2 is the correlation coefficient adjusted for the addition of parameters. Parameters in bold were found to be statistically significant ($p<0.05$).

Site	*Metal*	*Model*	*Rank*	*Wi*	*ΔAICC*	*R^2*
Rock Creek	Hg	Hg ~ 0 + 0.2654**T** +-0.7443 **Q** + -0.3343**SC** + 1.303**TURBIDITY**	**1**	0.30	0	0.78
		Hg ~ 0 + -0.9159**Q** +-0.4187 **SC** + 1.271**TURBIDITY**	**2**	0.15	1.41	0.74
	Pb	Pb ~ 0 + 0.1999Q + -0.4503**SC** + 0.4118**TURBIDITY**	**1**	0.28	0	0.89
		Pb ~ 0 + -0.4662**SC** + 0.5661**TURBIDITY**	**2**	0.25	0.29	0.88
Watts Branch	Hg	Hg ~ 0 +-4.739e-01 **Q** +1.350e+00 **TURBIDITY**	**1**	0.78	0	0.93
Hickey Run	Cd	Cd ~ 0 + 8.372e-01**SC** + 1.878e-01**TURBIDITY**	**1**	0.39	0	0.74
		Cd ~ 0 + 1.261e-01T + 8.860e-01**SC** + 2.401e-01**TURBIDITY**	**2**	0.24	1.00	0.74
	Hg	Hg ~ 0 +-4.093e-01 **SC** + 5.708e-01**TURBIDITY**	**1**	0.51	0	0.74

Temperature, discharge, specific conductance and turbidity were all significant predictor variables. The highest contribution was from turbidity, which showed a positive relationship with mercury. The best lead model for Rock Creek according to the AIC explained 89% of the variability of lead and had an evidence weight of 28%. Specific conductance and turbidity were significant continuous variables with the highest contribution from specific conductance. The model indicated a positive relationship between specific conductance and predicted lead.

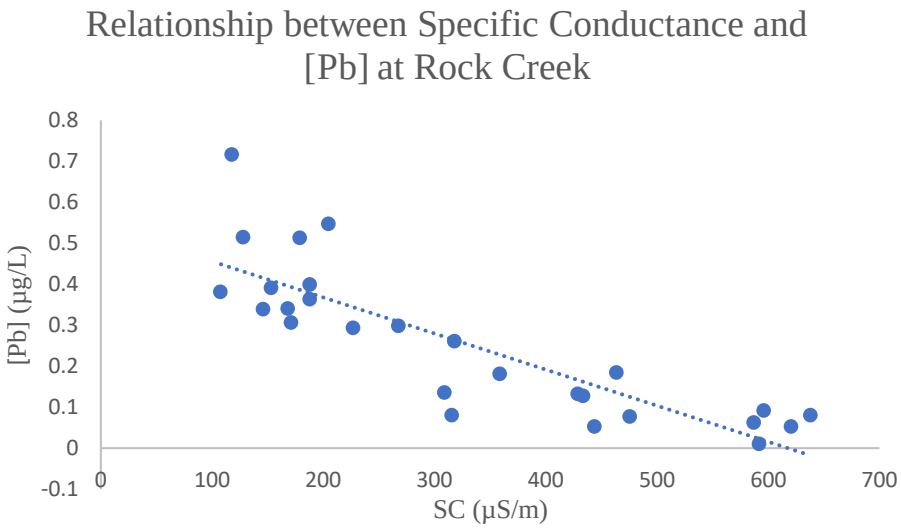
For the Watts Branch site, the best mercury model using multiple linear regression and AIC had a correlation coefficient (R_2) of 0.93 and an evidence weight of 78% (Table 6). Discharge and turbidity were the two significant continuous variables with the highest contribution (highest predictor variable coefficient) from turbidity. The best mercury model indicated a positive relationship between turbidity and unfiltered mercury concentrations.

The best multiple linear regression model for cadmium for Hickey Run explained 74% of the variability in cadmium concentrations and had an AIC evidence weight of 39% (Table 6). Turbidity and specific conductance were the only significant continuous variables with the highest contribution from specific conductance. The multiple linear regression model indicated a positive relationship between specific conductance and cadmium and between turbidity and cadmium. For mercury, the best multiple linear regression model had a correlation coefficient of 0.74 and an evidence weight of 0.51. Turbidity and specific conductance were also the only significant continuous variables with the highest contribution from turbidity. The best multiple linear regression model for mercury indicated a positive relationship between turbidity and specific conductance.

Evaluating Proxies for Metals using Individual Sensors

For comparative purposes, the most robust multiple linear regression model as indicated by the R_2 for each site was tested against a data set of metals not used to make the model (*i.e.*, the most recent data collected post May 2018). Using the multiple-sensor approach resulted in predicted values that varied significantly from the actual values, despite the high correlation coefficients of the models. This was true for all models. A single sensor approach was also then analyzed to assess predictability of metals concentrations and was proven to be more effective. Linear regression models were developed using significant sensors from the more robust multiple linear regression model for all locations (Table 6). For instance, a linear regression model developed from specific conductance was used to predict Pb concentrations in Rock Creek (Figure 8).

Figure 8. Relationship between specific conductance and lead concentrations at the Rock Creek watershed (R_2 = 0.71).



The resulting predicted values' percent differences from actual values were within 40% for some mid-range metals concentrations for the linear regression model relating specific conductance and Pb concentrations (Table 9).

Table 9. Percent differences below 40% between predicted and actual Pb concentrations for the linear regression model displayed in Figure 8.

[Pb] (µg/L)	Predicted [Pb] (µg/L)	Percent Difference (%)
0.29	0.34	15.04
0.13	0.16	17.74
0.40	0.38	6.06
0.22	0.27	15.61
0.13	0.15	19.48
0.39	0.41	4.05
0.51	0.43	18.12
0.30	0.30	1.53
0.36	0.38	3.15
0.51	0.38	28.90
0.11	0.12	12.29
0.52	0.46	11.46
0.49	0.43	14.82
0.25	0.22	10.03

Similar linear regression models were developed for metal fluxes using discharge as the predictive variable (Figure 9-10) with correlation coefficients ranging from 0.8 to 0.95.

Figure 9. Linear regression model for discharge and Cu flux at the Rock Creek watershed (R^2=0.95).

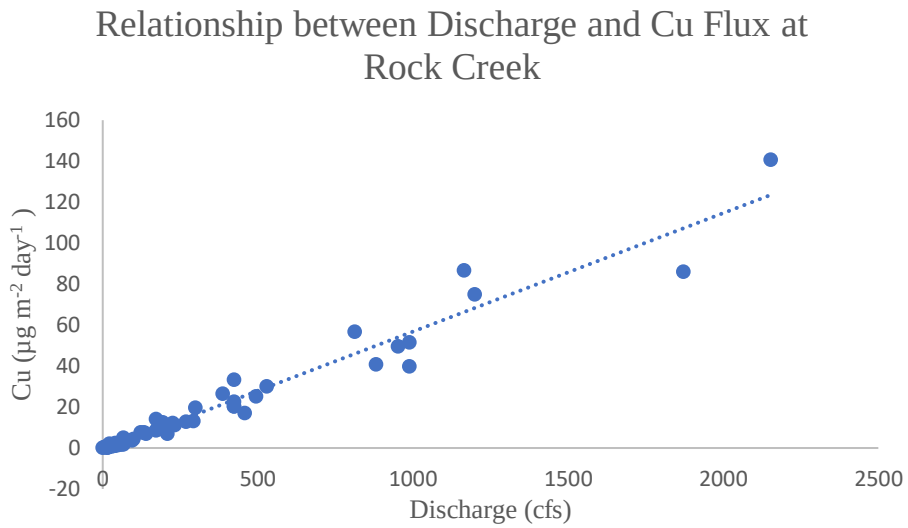
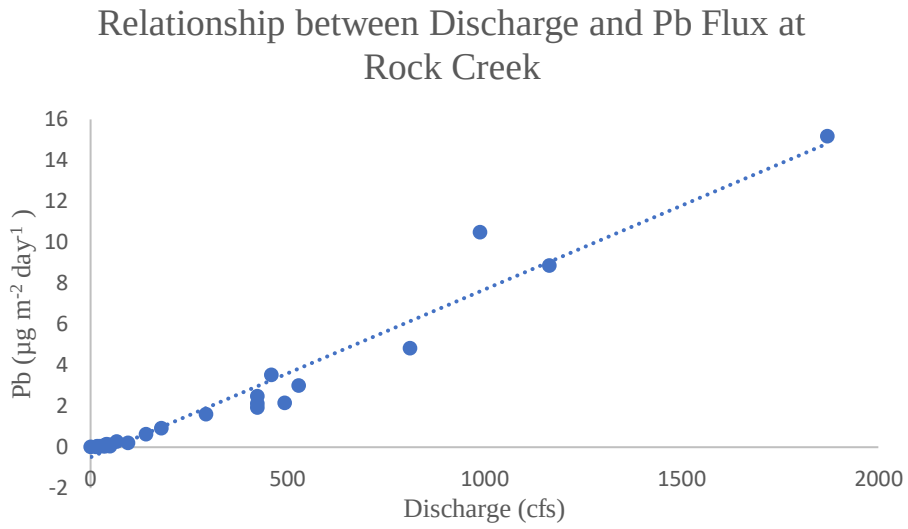


Figure 10. Linear Regression Model for discharge and Pb flux at the Rock Creek watershed (R^2=0.95).



Predicted metal fluxes were within 40% of actual values for mid-range fluxes; the model did not predict fluxes as well for low and high range values (Figures 9-10, Tables 10-11).

Table 10. Percent differences below 40% between predicted and actual Cu fluxes for the linear regression model displayed in Figure 9

Cu Flux (µg m^{-2} day^{-1})	Predicted Cu Flux (µg m^{-2} day^{-1})	Percent Difference (%)
18.44	24.67	28.93
10.88	13.63	22.45
4.57	5.37	16.09
1.70	1.38	-21.05
5.75	6.23	8.13
8.82	9.12	3.34
1.99	1.78	-11.14
0.88	0.92	3.89
3.44	3.98	14.44

Table 11. Percent differences below 40% between predicted and actual Pb fluxes for the linear regression model displayed in Figure 10

Pb Flux	Predicted Pb Flux	Percent Difference
3.42	4.59	29.30
4.77	6.14	25.08
2.42	2.95	19.48
3.55	3.33	6.40
0.62	0.66	6.24
1.56	1.89	18.98
14.13	14.68	3.83
0.70	0.95	30.47
0.25	0.22	14.72

The p-values of the simple linear regression models are displayed in Table 12. Some of the stronger relationships were plotted in Figure 11.

Table 12. Simple Linear Regression models for the Rock Creek, Hickey Run, and Watts Branch watersheds.

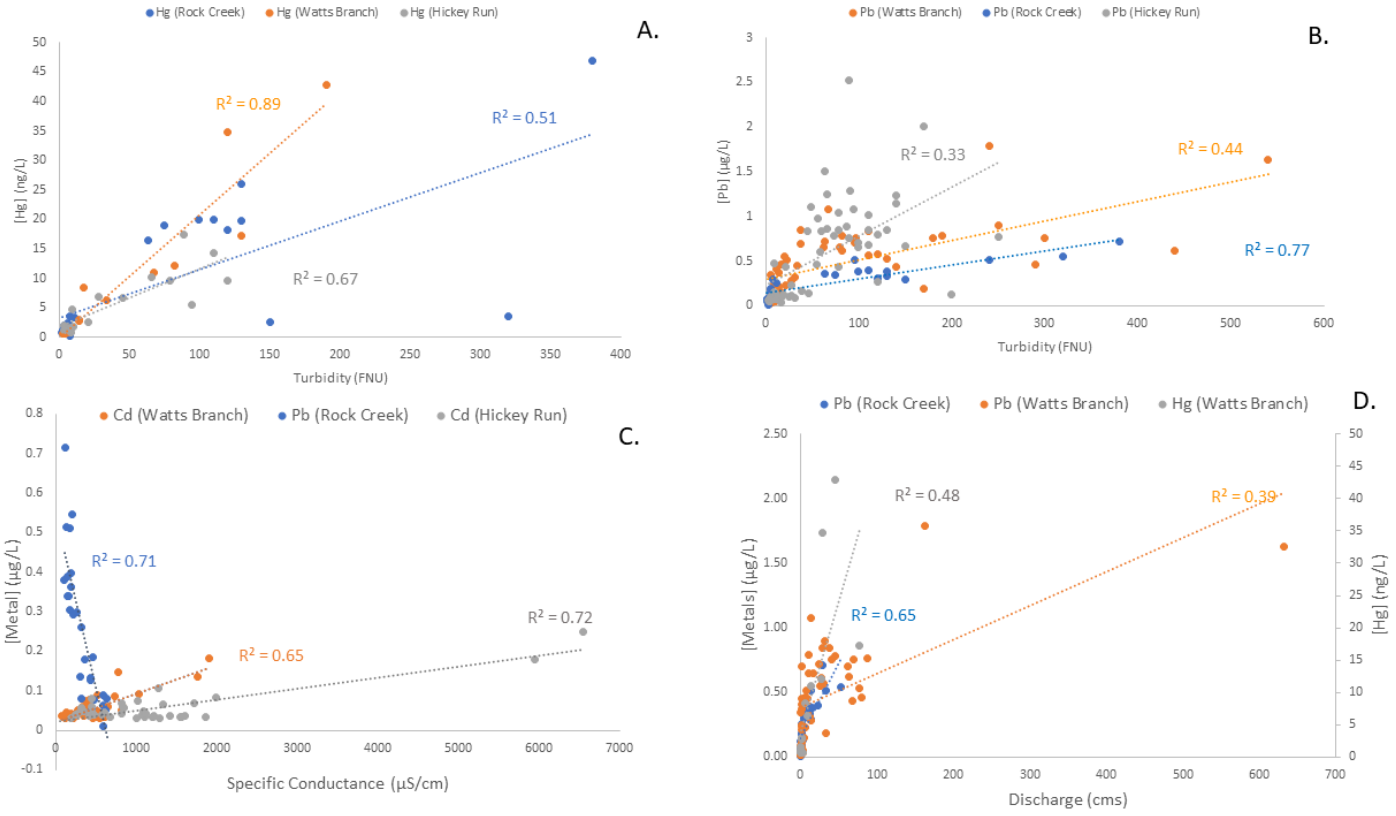
Site	*Metal*	*Model*	R^2	*p-value of x variable*
Rock Creek	Pb	[Pb]~ -0.0009 SC + 0.5438	0.71	2.88E-08

		[Pb]~ -0.0106 T + 0.4714	0.06	0.20
		[Pb]~ 0.0118 Q + 0.1473	0.65	3.38E-07
		[Pb]~ 0.0016 Turbidity + 0.1398	0.77	1.73E-09
		[Pb]~ -0.6669 pH + 5.1957	0.67	1.67E-07
		[Pb]~ -0.0132 DO + 0.3601	0.01	0.70
	Cu	[Cu]~ -0.2051 DO + 4.8741	0.14	1.36E-03
		[Cu]~ 0.033 T + 2.4815	0.04	0.12
		[Cu]~ 0.0344 Q + 2.7690	0.14	1.85E-03
		[Cu]~ -0.0006 SC + 3.2965	0.07	0.03
		[Cu]~ 0.0018 Turbidity + 2.9116	0.04	0.10
		[Cu]~ -1.6311 pH + 15.1485	0.19	1.64E-4
	Hg	[Hg]~ 0.0822 Turbidity + 3.3731	0.51	9.53E-05
		[Hg]~ -0.0051 T + 9.1249	0.00	0.99
		[Hg]~ 0.4456 Q + 5.2866	0.22	0.02
		[Hg]~ -0.0468 SC + 24.5703	0.49	1.29E-04
		[Hg]~ -3.8013 DO + 38.7326	0.10	0.13
		[Hg]~ -36.1569 pH + 277.9358	0.44	3.52E-04
	Cd	[Cd]~ -0.0006 Q + 0.0585	0.12	0.11
		[Cd]~ 0.0011 T + 0.0359	0.06	0.26
		[Cd]~ 7.2879E-06 SC + 0.0471	0.04	0.36
		[Cd]~ 0.0011 DO + 0.0452	0.01	0.76
		[Cd]~ -5.175E-05 Turbidity + 0.0563	0.05	0.33
		[Cd]~ 0.0238 pH – 0.1250	0.05	0.35
	Zn	[Zn]~ -0.1233 T + 4.7946	0.23	4.36E-03
		[Zn]~ -0.0034 Q + 3.2600	0.00	0.86
		[Zn]~ 0.0011 SC + 2.6680	0.24	3.84E-04
		[Zn]~ 0.1531 DO + 1.7677	0.07	0.12
		[Zn]~ 0.0007 Turbidity + 3.1474	0.00	0.70
		[Zn]~ 0.0988 pH + 2.4932	0.00	0.90
Watts Branch	Pb	[Pb]~ 0.0022 Turbidity + 0.2937	0.44	1.34E-07
		[Pb]~ 0.0037 T + 0.4225	0.00	0.64
		[Pb]~ 0.0026 Q + 0.3847	0.39	8.42E-07
		[Pb]~ -5.36E04 + 0.7053	0.25	1.97E-04
	Cu	[Cu]~ -0.0017 SC + 4.3045	0.05	0.076

		[Cu]~ -0.0313 T + 4.0241	0.01	0.48
		[Cu]~ 0.0015 Q + 3.5062	0.00	0.70
		[Cu]~ 0.0024 Turbidity + 3.3754	0.01	0.41
	Hg	[Hg]~ 0.2084 Turbidity - 0.0295	0.89	5.35E-07
		[Hg]~ -0.3615 T + 16.4163	0.05	0.45
		[Hg]~ 0.4072 Q + 3.9954	0.48	6.31E-03
		[Hg]~ -0.0522 SC + 27.1644	0.39	0.02
	Cd	[Cd]~ 7E-05 SC + 0.0209	0.65	9.22E-10
		[Cd]~ -0.0029 T + 0.0978	0.36	5.93E-05
		[Cd]~ -4.094E-05 Q + 0.0578	0.02	0.46
		[Cd]~ -2.373E-05 Turbidity + 0.0581	0.00	0.65
	Zn	[Zn]~ -0.526 T + 16.42	0.38	2.44E-07
		[Zn]~ -0.0011 Q + 8.4643	0.00	0.91
		[Zn]~ 0.0070 SC + 5.2945	0.15	2.86E-03
		[Zn]~ -7.43E-4 Turbidity + 8.4827	0.00	0.92
Hickey Run	Pb	[Pb]~ 0.0055 Turbidity + 0.2292	0.33	2.72E-06
		[Pb]~ -0.0092 T + 0.7125	0.01	0.45
		[Pb]~ 9.1846E-04 Q + 0.5468	0.05	0.09
		[Pb]~ -1.259E-04 + 0.7070	0.07	0.04
	Cu	[Cu]~ 0.0205 Turbidity + 3.1597	0.23	1.37E-04
		[Cu]~ -0.0381 T + 5.0170	0.01	0.48
		[Cu]~ -0.0012 Q + 4.4684	0.00	0.63
		[Cu]~ -2.23E-04 + 4.6748	0.01	0.42
	Hg	[Hg]~ 0.0982 Turbidity + 1.7953	0.67	1.81E-04
		[Hg]~ 0.0700 T + 5.1329	0.01	0.76
		[Hg]~ 0.5338 Q + 3.5426	0.42	0.01
		[Hg]~ -0.0099 SC + 13.4705	0.57	1.08E-03
	Cd	[Cd]~ 3E-05 SC + 0.0227	0.72	1.81E-11
		[Cd]~-0.0024 T + 0.0923	0.12	0.04
		[Cd]~ -1.329E-04 + 0.05790	0.00	0.85
		[Cd]~ 1.7317E-04 + 0.0449	0.06	0.15
	Zn	[Zn]~ 0.0672 Turbidity + 6.7805	0.24	8.77E-05
		[Zn]~ -0.2317 T + 14.50	0.03	0.18

	[Zn]~ -2.9576E-03 + 11.0529	0.00	0.70
	[Zn]~ -2.776E-06 +10.9736	0.00	1

Figure 11. Simple Linear Regression Relationships across the Rock Creek, Hickey Run, and Watts Branch watersheds.



For example, unfiltered mercury and filtered lead have strong linear relationships with turbidity across all sites (Figure 11 a-b) and specific conductance and discharge are also shown to have strong linear relationships with some metals across sites (Figure 11 c-d).

Discussion

As expected, concentrations and fluxes of trace metals increased with impervious surface cover and land development (*e.g.*, concentrations of mixtures in metals were typically greater in smaller watersheds with greater impervious surface cover). An increase in impervious surface cover in smaller watersheds could contribute to higher concentrations of metals in streams due to what is commonly referred to as the "first flush" effect (Protecting Water Quality from Urban Runoff, 2003; Lee and Bang 2000). The smaller watersheds could act as a sink for anthropogenic heavy metal accumulation on impervious surfaces and more efficient flushing of mixtures of metals on these impervious surfaces during hydrologic events (Protecting Water Quality from Urban Runoff, 2003; Lee and Bang 2000; Hunter et al. 1981; Weibel et al. 1964; Whipple and Hunter 1977). Thus, both smaller watershed size and increased impervious surface cover could contribute to increased 'hydrologic connectivity' and transport of metals (Kaushal and Belt 2012, Kaushal et al. 2020). Further work needs to be done to explore the effects of differences in the degree of hydrologic connectivity and potential impacts on variations in water quality across a broader gradient of urban watersheds.

Not only did concentrations and fluxes of metals vary with watershed size and impervious surface cover, but the composition of mixtures of metals also appeared to shift. We observed large temporal variability in the concentrations of metals in urban streams, sometimes by orders of magnitude, which were potentially due to changes in streamflow and other environmental variables. Discharge is a major component of flux, and it correlated strongly to daily fluxes of trace metals across study sites. We observed strong relationships between concentrations of the trace metals (Cu and Pb) and dissolved oxygen and between the trace metals (Cu, Pb, Zn, Cd, and Hg) and turbidity; there was also a sharp increase in some metals during winter months when road salt use and specific conductance increased (Cu, Pb, Zn, and Cd). These observations prompted us

to explore whether concentrations of metals such as lead, mercury, cadmium, copper and zinc could be influenced by sensor variables such as temperature, discharge, pH, specific conductance, turbidity, and dissolved oxygen in order to evaluate water quality.

The output from multiple linear regression analyses suggests that only some metals could be estimated from continuous variables. The metals, models, and amount of variation explained by a multiple linear regression model varied considerably among sites. In some cases, data from individual sensors could be used to predict metals concentrations, however. The usefulness of different environmental variables in proxy models of metal transport are explored below in addition to the implications of tracking chemical cocktails on urban water quality.

Variations in Metals Concentrations and Chemical Cocktails across Sites

Another factor contributing to variations in concentrations of metals across sites could be location and proximity to urban pollution sources; Watts Branch and Hickey Run gage stations are located in more urban settings with more anthropogenic sources of heavy metals. The Watts Branch gage station, in particular, is located in close proximity to a roadway and a railway. Even though parkland surrounds much of the Hickey Run gage station, it is located close to a major roadway. The Rock Creek at Joyce Road gage location, in comparison, is surrounded by acres of protected parkland and a U.S. National Park. Concentrations of metals could therefore vary across sites as some are located closer to anthropogenic sources of metals (*e.g.* major roadways).

Interestingly, we found that there were significant differences in mean metals concentrations across sites such as Cd, Pb and Zn, but not metals such as Hg and Cu using ANOVA (Table 5). Thus, the chemical mixtures and metal concentrations varied across sites. Some anthropogenic sources of these metals include smelting, waste incineration, combustion of fossil fuels, paint, roofing materials, leaded gasoline, tanning, pigment production, motor vehicles,

galvanized metal, batteries and mining (Bradl, 2005; Tchounwou et al., 2012; Ali et al., 2019). Metals related to automobiles may dominate the chemical cocktail in watersheds with greater hydrologic connectivity (Kaushal and Belt 2012). Our results from NMDS showed that not only do the concentrations of metals vary across the gradient of hydrologic connectivity, but so can the mixtures of metals.

Chemical cocktails of anthropogenic heavy metals can accumulate in urban soils and waters and can then accumulate in aquatic biota; this can increase effective toxicity of other anthropogenic chemical pollutants, and lead to pollution induced community tolerance. The study by Wheeler et al. (2005) included the impacts of metal laden urban runoff contamination on aquatic life. They found a pattern of elevated concentrations of lead, zinc and platinum in a variety of macroinvertebrates and fish that effected reduced taxa richness, reduced density of the biota, and lower functional diversity leading to overall community impairment in watersheds where urban land cover is greater than 40% (Wheeler et al., 2005). Salminen et al. (2009) modeled Zn pollution on soil microcosms and found that soils that had already been compromised by metals contamination; these soils had lower population growth of soil invertebrates and higher populations of pollution tolerant organisms (Salminen et al., 2009). Chemical cocktails of trace metals can enhance the effective concentration of other contaminants also. Yang et al. (2017) found that the addition of a chemical cocktail of cadmium, copper and lead significantly increased the mortality of zebrafish by increasing the effective toxicity and slowing the natural degradation of pyrethroids, a type of chiral insecticide (Yang et al., 2017). Urban metals contamination can not only have long-lasting, negative impacts on water quality for human use, but can impact species richness, food availability, fishing as a recreational sport, and even the complex soil microbial community. It is important to analyze a suite of metals from a “chemical cocktail” perspective

instead of analyzing for singular metals because metals can have a combined effect on overall health, as was shown in the Yang et al., 2017).

Comparing Metals Concentrations with Environmental Data from Multiple vs. Individual Sensors

There were some discrepancies in the expected relationship between the continuous variables and modeled relationships. For instance, specific conductance generally has a negative relationship with metals but in some models a positive relationship is shown. This could be a result of small sample size or changes in the relationship across seasons due to mobilization in winter from road salts. In addition, there is also some variability in the significant variables. In contrast, the individual sensor approach was able to predict some metals within reasonable ranges such as Pb and Zn at Rock Creek. This single sensor approach to developing proxies for metals concentrations is an alternative to the multiple-sensor predictive models. In some cases, a single sensor approach may be simpler to develop and thus more practical and adaptable across watersheds. The influence of different sensor parameters on metals concentrations is discussed below.

Discharge Influences the Fluxes of Metals across Urban Streams

Using the multiple linear regression (MLR) model, we found that discharge typically played a role in influencing the daily concentrations of mercury and lead at Rock Creek and Hg at Watts Branch, but not at Hickey Run. Dense, urban environments are abundant in sources of metal contamination that can be transported to local streams and rivers. The concentrations of metals in urban watersheds remains higher than reference watersheds, with the most common contributing factor being stormwater runoff (Charaklis et al., 1997; Franz et al., 2014; Lee et al., 2000; Mahler et al., 2005; Mason et al., 1998; Tiefenthaler et al., 2009; Wheeler et al., 2005). A major reason why urbanized watersheds have a higher concentration of metals contamination is that urban areas

have a much higher percentage of impervious surfaces that allow for contaminants to be transported to local streams and rivers *via* urban runoff. Metals from a variety of anthropogenic sources accumulate on these impervious surfaces and are transported directly to nearby streams during a rain event. Since impervious surfaces do not allow for the rain to percolate into the subsurface and because storm water systems act as channeled conduits for direct input into nearby streams, the erosional power of the storm water flow allows for greater transport of metals. In this study, samples for metals analyses were conducted across a range in streamflow conditions, including storms, which contributed to the large variability in concentrations at specific sites. During the "first flush," most of the metals that accumulate on impervious surfaces during a dry period are washed away in the first wave of runoff during a new rainfall (Protecting Water Quality from Urban Runoff, 2003; Lee and Bang 2000). The more mobile these metals and the more concentrated they become in local waters, the higher the chance of exposure and thus the higher the hazard or risk of the contaminant (Protecting Water Quality from Urban Runoff, 2003). Therefore, increasingly more frequent storm events that flush metals contaminants into local waters are a primary pulsed stressor that leads to a chronic issue of contamination in urban watersheds (Kaushal et al. 2014). Previously, it was noted that 84 percent of urban runoff ended up in rivers and streams (Wheeler et al., 2005). The Anacostia watershed, a transboundary watershed in D.C. and Maryland, was 54 percent urbanized in 1998 (Mason et al., 1998). As of 2012, the Anacostia watershed is nearly 70 percent urbanized and 23 percent of the watershed is impervious surface (DDOE, 2012). Urban storm water runoff accounted for 20-30 percent of Hg and methylmercury (MeHg) (a more mobile and bioaccumulative form of Hg) export into the Anacostia river in 1998 (Mason et al, 1998). A combination of impervious surfaces and storm

overflows could explain the strong positive relationship between discharge and metals concentrations and fluxes at Rock Creek, Watts Branch and Hickey Run.

Turbidity Influences Concentrations of Metals across Urban Streams

We found that turbidity played a significant role in influencing the concentration of most metals at Hickey Run in particular according to the MLR model. Many of the factors affecting discharge in urban stream environments also impact turbidity. Combined sewer and storm overflows can also contribute to the amount of suspended particulate matter or organic matter that contribute to overall turbidity in urban streams. Previous work has shown a significant and reliable relationship between total suspended solids (TSS) and turbidity in streams and rivers (Wagner et al., 2006, ASTM International, 2003). These solids will often adsorb as they contain functional surface groups that are able to complex with metals (Stumm and Morgan, 1996). Turbidity is strongly influenced by the properties of transported sediment, which varies in shape size and mineral composition (Yao et al., 2016). Desorption of weakly sorbed metals and transitions from sediment brought in after a storm to the aqueous dissolved state could explain elevated concentrations of dissolved metals with turbidity, even though one would expect a lower concentration of dissolved metals with an increase in turbidity and thus availability of particulate sorption sites. Indeed, Bourg 1987's conceptual model of adsorption and turbidity show that with increased turbidity, the percentage of adsorbed metals like Cu and Zn increases as a result of simple Le Chatlier's principle. Affinity for the solid phase also appears to increase with increasing organic matter content (Mouvet and Bourg 1983). The suspended particulates associated with turbidity in Rock Creek, Hickey Run and Watts Branch could be courser material low in organic matter.

Specific Conductance Influenced Metals Concentrations with Differing Seasonal Patterns

Interestingly, we found that specific conductance played a role in influencing the concentrations of mercury and lead at Rock Creek based on the MLR model. There was also an interesting seasonal increase in all metals except Hg during winter months when specific conductance simultaneously peaked, which suggested mobilization of metals associated with road salts (Kaushal et al. 2019). Recently, it has been recognized that salt pollution in urban watersheds can contribute to Freshwater Salinization Syndrome, which is the suite of interrelated water quality impacts associated with salinization such as ion exchange and metals and nutrient mobilization (Kaushal et al. 2018, Kaushal et al. 2019). As the salinity of a solution increases, the solubility of a nonpolar or weakly polar organic compounds decreases because the organic compound is now competing with ionic species that are much easier for the water to solubilize. The salting-in relationship can also be defined with the Setschenow equation, meaning the solubility of the compound is dependent on the concentration of the salt or salts (Bockris et al., 1950). The salting-in effect is the increase in solubility of compounds in solution. In the case of metals, it is most related to the formation of more soluble complexes thorough anion-complexation, mentioned also as simple coulombic attraction (Du Laing et al., 2008). Chlorocomplexation with cadmium, for example, decreases the activity of Cd^{2+} adsorbed in the sediment and increases the solubility and thus mobility of the heavy metal (Hirsh et al., 1990). Cd-chlorocomplexes are also highly stable. Divalent cations from salts such as Ca^{2+} and Mg^{2+} can also work to compete with metals like Zn and Cd adsorbed to sediment, mobilizing them in solution (Du Laing et al., 2008). These two processes were found to control a large variance in reversible cadmium portioning between suspended sediment and solution, accounting for a large variance in cadmium mobility under controlled laboratory conditions meant to simulate natural conditions (Rob et al., 2008). With other metals such as Fe^{3+}, chloride can serve as a catalyst for the reduction of Fe^{3+} to Fe^{2+} (Sutin et al.,

1961). In addition, some salts with anions from weak acids generate a more basic solution, allowing for metals to precipitate out of solution.

Dissolved Oxygen Weakly Influenced Metals Concentrations but Showed Patterns with Cu

Dissolved oxygen was significantly related to Cu concentrations when analyzing relationships between concentrations and individual DO sensor data at Rock Creek according to a regression analysis ($p<0.05$). However, dissolved oxygen was a weak predictor and was taken out of the Rock Creek model due to intercolinearity as reported by the *vif* function. While the trends in the data show a weak negative relationship between dissolved oxygen and Cu, dissolved oxygen has a complex relationship with metals in regards to adsorption and release. Li et al. (2013) observed release of Zn, Cu, Cr and Pb increased under aerobic conditions while the adsorption of metals and release of Cd occurred under anaerobic conditions. During reducing conditions, co-precipitated metals with Mn and Fe oxides were also found to be released and at stronger reductive conditions sulphide can complex with metals and reduce mobility (Li et al., 2013). Li et al also found greater adsorption of metals at lower DO concentrations than at higher DO concentrations possibly resulting from adsorption to iron and manganese (hydr) oxide solid phases and sulphide complexation. In contrast, Kang et al. (2019) showed that that Pb, Zn and Fe were released from sediments in an anoxic environment and adsorbed from the overlying water in an aerobic environment. They found that adsorption onto surfaces of iron and manganese oxy-hydroxides occurred more in oxidizing conditions and metals were released under reducing conditions. Thus, higher dissolved oxygen better facilitated release of metals than lower dissolved oxygen conditions.

Conclusions and Monitoring Implications

The impact of urbanization on the transport and transformation of multiple metals in urban streams has led to a need for tracking the constituents of this chemical cocktail more holistically. Using multiple linear regression approaches, our analysis suggests that assessing metals concentrations from continuous variables only is effective for some metals at some sites. However, there were cases where data from individual sensors showed relatively strong statistical relationships with trace metal data. One potential implication is that more continuous sensor variables should be considered for additional and more diverse measurements to try to explain more of the variation in metals concentrations. Difficulty in applying some sensors to predict metals concentrations in some cases could also be the result of a limited sample size for discrete characterization of stream water chemistry for grab samples. Furthermore, the metals data (with the exception of mercury) is represented by free or dissolved metals. Perhaps, analysis of total metals would produce better correlations with more continuous sensor variables. Future work could focus on augmenting current data sets with collection of dissolved and total metals data and additional sensor data to create more robust predictive models that could eventually serve to streamline the process of assessing water quality with regards to metals. Overall, results from continuous environmental sensors can help inform monitoring and management efforts for metals in urban streams. Use of sensor data to develop predictions would not replace the importance of direct measurements of metals concentrations *via* grab samples and traditional analyses using ICP-MS and ICP-OES. Rather, it could help predict data sets at a higher-frequency temporal resolution and assess whether more time-consuming and costly measurements should be employed based on using statistical models. For future predictor models with low correlation coefficients, further research should include utilization of more predictor variables and expanding the calibration range of current sensors.

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